TIGHT-BINDING STUDY OF Si_2C_n (n=3 to 42) FULLERENE-LIKE OR NANODIAMONDS MICROCLUSTERS: ARE Si ATOMS ISOLATED OR ADJACENT?

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We studied in tight-binding approximation involving sp^{ν} hybridization (ν=2,3), some Si2Cn (n=3 to 42) microclusters. We then investigated, on one hand, fragments of fullerene-like structures (sp^2) , and on the other hand, nanodiamonds (sp^3) of adamantane-type or a 44-atom nanodiamond (with 2 inner atoms which are assumed to play the role of bulk atoms).We compared the stabilities, i.e. the electronic energies of these clusters, according to the various positions of the 2 Si atoms.Results are very different in the two kinds of hybridization. Besides, they can be analysed according to two different points of view: either the clusters are considered as small particles with limited sizes, or they are assumed to be used as models in order to simulate the Si-atom behaviour in very larger systems. In sp^2 hybridization (fullerene-like geometries), the most stable isomer is always encountered when the 2 Si atoms build a Si2 group, and this result holds for both viewpoints quoted above.Conversely, in sp^3 hybridization (nanodiamonds), since Si atoms "prefer" sites having the minimum connectivity , they are never found in adjacent sites. We see that with a simple and fast computational method we can explain an experimental fact which is very interesting such as the relative position of two heteroatoms in the cluster. This enhances the generality and the fecondity in the tight binding approximation due essentially to the link between this model and the graph theory, link based on the topology of the clusters.

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I.Introduction

Silicon carbides are generally encountered as industrial materials known for applications in high-temperature ceramics or semi-conductors. Silicon carbide microclusters are produced in many experiments : SIMS (secondary ionic mass spectrometry), SSMS (spark source mass spectrometry), LAMMA (laser microprobe mass analysis), etc. They can be also found in interstellar or circumstellar space.

In mixed silicon-carbon nanoclusters as those generated in a laser vaporization source [1], an interessant question can be asked: do the silicon atoms "prefer" to be adjacent, or isolated as in linear SiCnSi chains? Some studies on Si2C58 heterofullerenes lead to think that silicon atoms seem to "prefer" to be adjacent rather than isolated in the carbon "network" [2,3].

Carbon and silicon belong to the same column IV-B of the periodic table. However, their structures in the solid state are different. Carbon indeed can be found in several allotropic varieties such as diamond, graphite, or linear chains observed in the interstellar space such as molecules HC_nN (carbyne phase [4]) whereas silicon is always found in three-dimensional systems.

In mixed silicon-carbon Si_pC_n nanoclusters, we previously pointed out that experimental results show a progressive transition from a carbon-type behaviour (with enhancement of C_n^+ ion currents for odd n: SSMS [5]) to a silicon-type behaviour (in which the Si_p^+ ion currents are maximum for even p) in proportion as the silicon richness is growing in the clusters [6]. It can be derived from the above results that in ions such as $Si\ C_n^+$ or $Si_2\ C_n^+$, silicon follows the behaviour of carbon atoms and adopts their structures and conversely in silicon-rich ions as $Si_3\ C_n^+$ or $Si_4\ C_n^+$, carbon atoms behave as silicon atoms.

Many studies have been carried out on very small species such as SiC_3 and Si_2C_2 using *ab initio* methods [7], or Si_pC_n ($n+p<6$) from both experimental and theoretical points of view [6,8-9], in order to determine the structure and geometries of the clusters.

So, the remaining question is: in Si_pC_n microclusters (especially fullerenes) , do the silicon atoms « prefer » to be adjacent, or « isolated » as in linear SiC_nSi chains [7,9] ?Is it possible with the tight binding approximation to answer this question on the relative positions of two heteroatoms? The results reminded above are about fullerenes, therefore essentially the sp^2 hybridization as we will see it. But, what about the position of Si pairs in the sp^3 hybridization, i.e. in a cubic diamond structure? In this aim, we studied some Si_2C_n (n=3 to 42) microclusters in tight-binding approximation involving sp^ν hybridization (ν=2,3),

We first present the calculation method, then the various kinds of geometries. For every shape of cluster, we determined the position of the 2 silicon atoms which leads to the largest stability. Moreover, the cases of larger clusters are also used to simulate the behaviour of 2 silicon atoms embedded in the bulk and consequently to find the preferential positions of 2 impurity atoms in a carbon matrix.

II. Fundamental assumptions of the tight binding approximation with hybridization

This calculation method was initially built for covalent solids with carbon atoms in sp^3 hybridization (cubic diamond lattice). We made this model suitable for finite systems such as microclusters of group IV-B elements with possibly including heteroatoms, in the other kinds of hybridization, sp and sp^2. In these last cases, the π bonds are separately treated in the « usual » Hückel approximation (cf Appendix).

Let us recall the main hypotheses. We only consider the four valence atomic orbitals (AO) (2s, $2p_i$ for C, 3s, $3p_i$ for Si, i=x,y,z).

II. 1.sp^ν hybridization

In sp^ν hybridization (ν=1,2,3), there are four hybrid orbitals per atom (C or Si) built by linear combinations (LCAO) of the above s and p AOs, that is (ν+1) sp- or σ-hybrid orbitals along the bond between 2 neighbour atoms, and (3-ν) π-orbitals orthogonal to the bond.

The sp hybridization is dealing with linear open-chain (1D) or closed-ring molecules. The plane geometries (2D) can be studied in sp^2 hybridization. 3D-geometries need sp^3 hybridization with per atom, 4 sp- or σ-hybrid orbitals directed toward the apices of a tetrahedron (cubic diamond lattice).

II. 2.Partition of the hamiltonian according to σ or π orbitals (in sp ou sp^2)

The partition of the hamiltonian is valid since we are in the " one-electron approximation ", and leads to two independant hamiltonians : sp hamiltonian and π hamiltonian. The hamiltonians are given in the Appendix.

The σ or sp hamiltonian describes the skeleton of the cluster bonds. In the following, the clusters are named after the skeletons of the corresponding hydrocarbons (the name of which are detailed in Streitwieser [10]), but the clusters do not include any hydrogen atom ; they are built only with carbon atoms and doped with two silicon atoms as heteroatoms. Hydrogen atoms of the hydrocarbons are then here replaced by « dangling bonds ».

The π hamiltonian is dealing with delocalized electrons: π AOs are perpendicular to the molecular plane if it is a 2D-molecule (however pieces of fullerenes are not actually planar molecules because of the presence of pentagons, but we consider them as if they were of planar-type ones) or to the molecular backbone if it is a linear one in sp hybridization.

The electronic energie of a cluster is deduced by diagonalizing the hamiltonians and filling in the energy levels with all the valence electrons. The origin of the energies is taken as usual at the « vacuum level ».

However, an important restriction has to be brought: in our model indeed, neither the repulsive energies between the nuclei nor the dielectronic correlations are clearly taken into account. In fact, averaged values of these contributions are included in the parameters of the model such as β_σ or β_π, the usual resonance integrals (Appendix) used in the hamiltonians. Nevertheless, the results of our calculations are validated by comparison to the results of *ab initio* calculations on some very small clusters.

Due to this restriction, in order to determine which clusters are the most stable ones for a given number of atoms n, we are only able to compare the electronic energies of clusters with the same number of bonds.

II. 3.The silicon atoms are assumed to be in the same hybridization as the surrounding carbon atoms.

The assumption is supported by the experimental results we recalled above in introduction since we are dealing with Si_2C_n nanoclusters, that is with few silicon atoms.

As a summary, we used a semi-empirical method which is validated by the comparison with ab

initio computations or Density Functional Theory computations, but which is infinitely faster due to the very small number of parameters which are necessary (see Appendix); our method allows us to examine a very large number of isomers, in particular when comparing the electronic energies of all the possible positions of the two Si atoms in a given cluster, or for several geometries. This method may lead to the study of the more stable geometries in the case of more sophisticated computations (as a first test or for a large number of atoms). The tight binding model (or Hückel model) has been used for small metal clusters and gave similar results to those of local-spin-density and configuration interaction calculations [11]. Moreover, this model shows that there is a connection between the stability of a cluster and its topology.

III.Investigated geometries

III. 1.Fullerene-like clusters

The fullerenes are exclusively built with pentagons and hexagons. We have then studied fragments of fullerenes, that is shapes showing combinations of these polygons, with the same number of bonds for a given number of atoms, in order to be able to compare the stabilities which are in fact represented by the electronic energies, as written above.

The normal bond angle is 109°28' in sp^3 hybridization and 120° in sp^2 ; so the hybrid orbitals are strongly directed. The bond angle at a vertex of a regular pentagon is 108°, thus very close to the "natural" angle between two sp^3 hybrid orbitals, while the 120°-angle is the "natural" angle in an hexagon (sp^2) : sp^2 orbitals are directed toward the apices of an equilateral triangle. This is the second reason why we have exclusively considered these 2 kinds of polygons in the studied agreggates. Strained shapes are not taken into account.

We can remark that if graphite is composed of planes of hexagons, that is in sp^2 hybridization, the introduction of one pentagon in such a plane, tends to bend the foil of graphene by creating a

default, that is a disinclination of 60° ; it is indeed impossible to cover a plane only with pentagons. It is known that twelve pentagons among several hexagons, are enough to give a complete sphere (Euler theorem[12]).

Therefore, the clusters which we studied are not really flat, so that the atoms are not in pure sp^2 hybridization, but have a partial sp^3 character. Let us recall that calculation shows that C_{60} has about ten per cent of sp^3 character [13]. However, our calculation method is built with the above approximations. Besides, the tight binding approximation, derived from the Hückel theory, is a topological-type method connected with graph theory, which only deals with the bonding between first-neighbour atoms, but neither with the bond lengths nor with the bond angles. This relationship have already been pointed out by Wang et al [11] in their studies on geometry of small metal clusters: they show a close connection between the stability of a cluster and its topology. In our case, it is a little more complicated due to the presence of s and p electrons.

Accordingly, it does not seem necessary to take into account the defaults in the flatness of the clusters only constituted of fragments of fullerenes. And we shall assume that all the atoms including silicon atoms are in sp^2 hybridization.

Sandré and Cyrot-Lackman [14] have built a tight-binding method using only p_z AOs (equivalent to our π orbitals) in order to take into account the bending of the hexagon planes in the calculation of carbon nanotube structures. In our case, the clusters are small enough to neglect the bending induced by the presence of one or two pentagons. Besides, since we are studying clusters in sp^2 or sp^3, we have to use 4 AOs per atom as written above, without restricting ourselves to the π orbitals.

We dealt with clusters of various sizes in sp^2, especially Si_2C_{14}, fragments of fullerene such as Si_2C_{16}, Si_2C_{18}, Si_2C_{28} or clusters with hexagons and 2 pentagons (Wakabayashi cluster [15]) , coranullene and several clusters with « condensed rings » (see Figures 1 to 4).

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III.2 .Nanodiamonds

We investigated as nanodiamonds, clusters in sp^3 hybridization, i.e with the structure of the cubic diamond lattice. The smallest one is:

- adamantane Si_2C_8 which we used as a unit block to build some bigger clusters (Fig.2)
- "double adamantane" Si_2C_{12},
- "triple adamantane" Si_2C_{16}.

However, since these clusters only contain "surface atoms" with many dangling bonds, we also built

- a 44-atom nanodiamond Si_2C_{42}, deduced from the Chelikowsky 35-atom cluster [16] by adding atoms in order to have 2 inner atoms (instead of one in the 35-atom cluster) able to play the role of bulk-atoms.

We studied all these aggregates from 2 points of view:

- <u>their general stability</u>, i:e:

1. where, in a given cluster, the Si atoms are preferentially found ? Are they in first-neighbour sites, that is: are they adjacent, or second- or third-neighbour sites ?

2. what is the most stable shape for a given number of atoms in the clusters, and for a given number of bonds?

- <u>as model for larger clusters</u>

in a fullerene or in diamond lattice, are the Si atoms rather adjacent or not?

For every cluster, the hamiltonians are built according to the above hypotheses and diagonalized, which gives the energy levels; electronic energy of the cluster is obtained by summing the energies of the occupied levels. Comparison of clusters of given atom numbers having

the same bond numbers enables us to avoid taking into account the nuclear repulsion energy.

IV.Results

IV.1. Stabilities and simulation of the bulk

The results are shown for fullerene-like clusters in figures 1 to 3 and for the nanodiamonds in figure 4. We have then considered clusters Si_2C_n with n going from 3 to 28 in sp^2 or from 8 to 42 in sp^3 hybridization, with various shapes, and we have been able to draw some simple rules.

IV. 1.1.Hybridization sp^2

The first results shown in figures 1 a, b, c, d, and e, are the following, in all cases except for n=20 (a), the 2 silicon atoms are neighbours and on external sites of the cluster. This generalizes our results on silicon atoms for XC_n clusters [17] following which if the heteroatom X is less electronegative than the carbon (case of Si), the X atom is preferentially found on the site with minimum connnectivity, i.e.with a minimum number of bonds suitable with the shape of the cluster, while if X is more electronegative than C (as is the case of N for example), the heteroatom X is found on sites with a maximum connectivity (3 in the sp^2 hybridization)

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Moreover, when the cluster includes at least one pentagon within a set of condensed-rings, the 2 atoms of silicon are found on the 2 neighbouring apices of the pentagon, except when the pentagon has only one or no apex with a dangling bond as is the case for : n=11 (b), 13 (b), 14 (f,g), 16 (a), 18 (b,c), 20 (a) et 28 (a,b). In the latter cases, the Si atom is found on an hexagon with an apex linked to a dangling bond.

Furthermore, the clusters containing one pentagon are often more stable than the clusters without

one, on condition that this pentagon is not completely embedded within the cluster. This may be clearly understood by the fact, already noticed above, that the bonding angle of 108° in the pentagon which is very close to the angle of sp^3 hybrids. This may be called the « pentagon rule ». Indeed,in figures 1, the shape n=11 (a) (pentanaphtalene) which contains one external pentagon is more stable than the perinaphtenyle (c) which has 3 condensed hexagons. But, the shape (b) though it contains one pentagon, is the less stable within a,b,c because the pentagon is embedded within the cluster and has only one free apex which prevents it from placing the 2 Si atoms in the pentagon. This last feature explains why the Si atoms cannot be found on this pentagon. Finally, the clusters with at least one pentagon are the more stable if the two Si atoms can be placed in it, thus if the pentagon contains at least two free apices. This is the case of n=18 (a).

In the particular case n=20 (a), each Si atom is found on the free apex of the pentagons, which leads to a very symmetrical shape. This may explain that the cluster n=20 (a) with 2 Si atoms far from each other is more stable than the shape (b) with neighbouring Si and with a lower symmetry order.

In the other particular case of bicyclic molecules, we observe that the more stable the cluster is, the less dissymetrical it is: indeed for n=9, the shape (a) (cycles 6/7) is more stable than the shape (b) (5/8) though 2 Si atoms are present in the pentagon.This is an exception to the « pentagon rule ».

IV.1.2. Hybridization sp^3

In the case of nanodiamonds, figure 2 shows the adamantane and the two clusters containing 2 then 3 adamantane groupments and the clusters with 44 atoms in which the positions of the Si atoms correspond to the most stable clusters. We see that these latter are always on the outer apices which have the greatest number of dangling bonds. Such apices are never adjacent.

IV.2.Models for larger clusters

In tables 1 to 4, we recalled the electronic energies for the Si_2C_n clusters in the cases n=28 et 30 in sp^2 and n=42 in sp^3, computed with several positions of the two heteroatoms, i.e.in first, second and third neighbours in order to compare their values and find the associations between the Si atoms which lead to the most stable clusters. To avoid all finite size effects, which is essential to simulate very large clusters which have the role of the bulk, we considered only the sites inside large clusters and with saturated bonds (3 in sp^2 and 4 in sp^3) leading to the choice of positions in Fig.3 and 4 marked with black squares or rhombuses.

IV.2.1.Hybridization sp^2

For Wakabayashi cluster (Table 1), the origins of the Si atoms pairs have been taken at sites 9, 2 and 10. The $|E_1|$, $|E_2|$, $|E_3|$ represent the absolute values of the pair energies respectively in first, second and third neighbours ,and the ΔE_i (i=2,3) are the energy differences between $|E_1|$ and $|E_2|$ or $|E_1|$ and $|E_3|$. We did not compute the pairs in the cases where a position has a dangling bond, for instance the pair 9/12 (which may correspond to the path 9-10-11-12).

Thus for the pair of second neighbours 9/7 (which corresponds to the dotted path 9-8-7 in Fig.3), the energy $|E_2|$ is lower of a value of 0.79 eV to that of $|E_1|$ which is the energy of first neighbours pairs 9/8. The difference is even larger for the energy of the pair 9/8 compared to that of third neighbours 9/1 (with the path 9-8-7-1) or 9/16 (with the path 9-8-7-16). The ΔE_i (in bold) are then positive, which indicates that the pair of first neighbours 9/8 corresponds to the most stable cluster.

In the tables the values of ΔE_i corresponding to a maximum of stability for the first neighbours positions are written in bold. We observe a few exceptions for which the ΔE_i (in italic) are negative, but only for the third neighbours positions, for example for the pairs 2/8 or 10/7. In each

of these cases, the Si atoms are in an hexagon on opposite sites; this may explain, for reasons of symmetry, a larger stability in this particular case.

For Wakabayashi cluster, we can conclude from this study that the pair 9/8 (energy in bold underlined) gives the largest stability for all investigated combinations. Straighforwardly, we have the largest probability to have two adjacent Si atoms on the edge of one hexagon joining two opposite apices of the pentagons in the cluster.

The same study is made for the half fullerene (Table 2) from the positions 3, 2 and 1. It shows that in all cases, the ΔE_i are positive, therefore that the cluster is more stable when the two Si atoms are first neighbours. The largest energy (bold underlined) corresponds to the pair 3/12 which is, as in the last case on the edge of an hexagon joining two pentagons.

In Table 3 is the case of "ovalene" Si_2C_{30} in order to simulate a part of graphene. (One may remark that ovalene may be deduced from the Wakabayashi cluster by replacing the 2 pentagons by 2 hexagons). The origin positions are in 1, 2 or 3. We observe that in most of the cases, indeed, the ovalene is more stable for two first neighbours Si atoms. The only third neighbours pairs which give negative ΔE_3 correspond to opposite Si atoms on an hexagon for example 2/5, or 3/6 or 1/4. The largest stability is obtained for the position 2/3.

Finally, it is only in the case of the half fullerene that the two Si atoms always give a larger stability for first neighbours pairs. For Wakabayashi cluster where the pentagons are external to the cluster and even more in the case of ovalene (with no pentagon), given third neighbours pairs may be more stable than first neighbours ones. Nevertheless, even in these last two cases, the position with the largest stability is one pair of Si atoms in first neighbour positions.

IV.2.2 Hybridization sp^3.

Because of the small size of the nanodiamonds which has been studied here (see figure 4), there are few positions corresponding to saturated atoms. This reduces the number of pairs that we may study as many atoms have only 3 saturated bonds and one dangling bond. We took as origin the sites 7 (more internal atom) and 5. Following Table 4, we see that in all cases, the second neighbours pairs give the largest stability. Thus, for 7/16 ou 7/19. Therefore the Si atoms are never first neighbours in the sp3 hybridization.

Let us remark, that we studied also fullerene clusters in a mixed hybridization with the Si atoms in sp^3 in a set of carbon atoms in sp^2. This leads to adding two dangling bonds to the system. The electronic energies are smaller than in a calculation in pure sp^2 hybridization, but the positions giving the most stable clusters remain the same ones. This shows that it is the general topology of the cluster which plays the leading role: fullerene type geometry or cubic diamond geometry.

V.Conclusion

In our study, we used a tight-binding method taking hybridization into account, in order to consider the first steps of formation of fullerenes or nanodiamonds containing silicon atoms as impurities.

First, for the stabilities of the aggregates, one important result in sp^2 is that, if there is one pentagon among an assembly of " condensed-rings ", the clusters are more stable, and the 2 Si atoms are preferentially encountered on the edge of a hexagon placed between 2 pentagons. This agrees with the "pentagon rule" we pointed out in the study of the XC_n clusters [17] which showed that if the heteroatom such as Si is less electronegative than C, it is always found in a pentagon except if there is no dangling bond on the pentagon; in this last case the Si atom is in a hexagon with at least one dangling bond on its apices. In the present case, because we have two heteroatoms which have to be

placed, we have some exceptions to the « pentagon rule ».

In sp^3 hybridization, clusters are the most stable ones when the Si atoms are placed on sites with the minimum connectivity.

Second, when large clusters (of 30, 32 or 44 atoms) in sp^2 or sp^3 are assumed to simulate larger systems, we found that in sp^2, the 2 silicon atoms are always in first-neighbour sites, especially when these sites belong to pentagons.

Conversely, in sp^3, there are never Si_2 pairs, but rather Si-Si in second-neighbour sites and preferentially in third-neighbour sites.

Finally, the general conclusion is that in sp^2 for fullerene-like clusters, we always observed the two silicon atoms in adjacent sites, whereas in sp^3, they are always isolated.

As a general conclusion, the tight binding approximation allows one to study the formation of heterofullerenes with a close link to their topology and geometry and is a fast computational method.These results obviously can be used as a first step for more sophisticated studies such as ab initio or DFT calculations.

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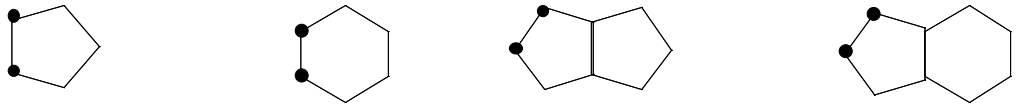
Clusters Si_2C_n in sp2 I

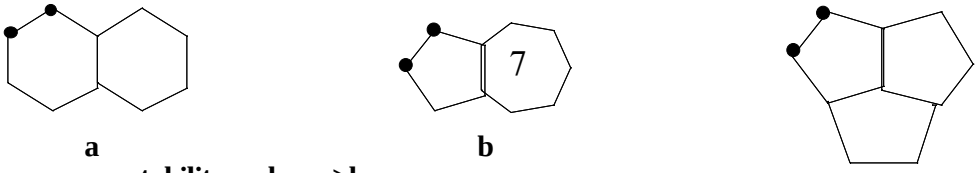
Si_2C_3 Si_2C_4 Si_2C_6 Si_2C_7



Si_2C_8

11 bonds **12 bonds**

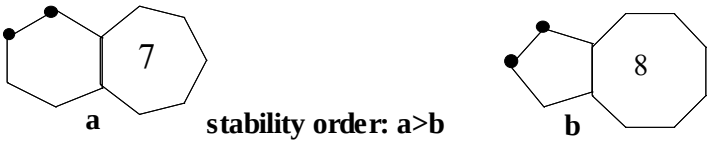
naphtalene azulene acepentylene



a **b**

stability order: a>b

Si_2C_9 **12 bonds**



a **stability order: a>b** **b**

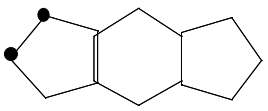
Si_2C_{10}

13 bonds **14 bonds**

1). 1 pentagon + 2 hexagons

a **b**

2). 2 pentagons + 1 hexagon



c

stability order: b>c

- atom Si

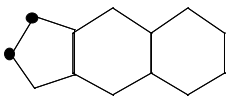
fig 1a

Clusters Si_2C_n in sp2 II

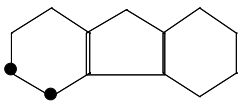
Si2 C11 - 15 bonds

1). *1 pentagon + 2 hexagons*

pentanaphtalene



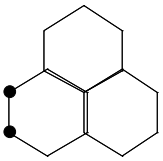
a



b

2). *3 hexagons*

perinaphtenyle



c

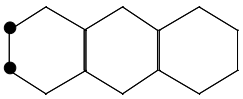
stability order: a > c > b

Si2 C12

1). 3 hexagons

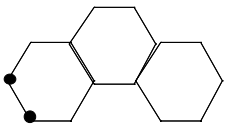
16 bonds

anthracene



a

phenanthrene



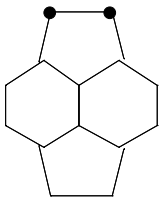
b

stability order: a > b

2). 2 pentagons + 2 hexagons

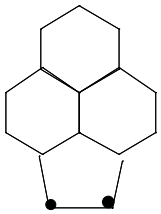
17 bonds

pyracylene

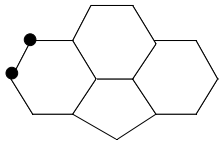


Si 2C13 - 18 bonds

1 pentagon+ 3 hexagons



a



b

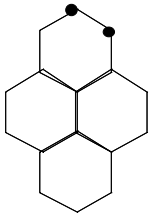
stability order: a > b

fig1b

Clusters Si_2C_n in sp2 III

Si2 C14 - 19 bonds

1). 4 hexagons

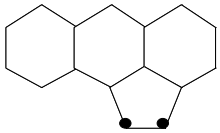


a

pyrene

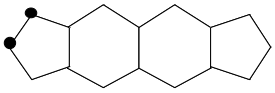
2). 1 pentagon + 3 hexagons

b

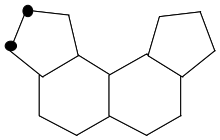


3). 2 pentagons + 2 hexagons

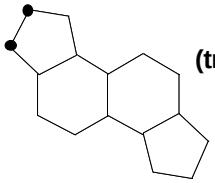
a).outer pentagons



c



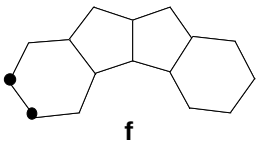
d
(cis)



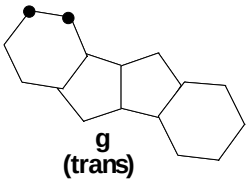
e
(trans)

b).inner pentagons

Stability order: b >= a > c > f > g > d > e



f
(cis)



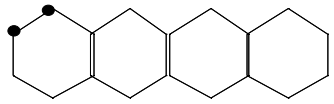
g
(trans)

Fig.1c

Clusters Si_2C_n in sp2 IV

Si_2C_{16} - 21 bonds

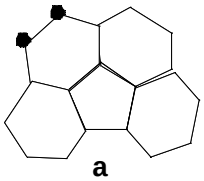
4 hexagons



naphtacene

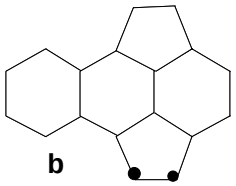
Si_2C_{16} - 22 bonds

4 hexagons + 1 pentagon



a

3 hexagons + 2 pentagons



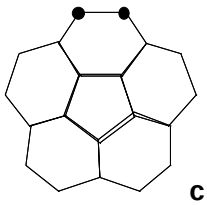
b

stability order: a > b

Si_2C_{18} - 25 bonds

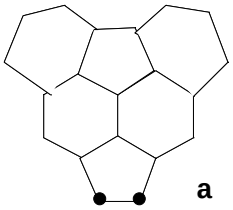
5 hexagons + 1 pentagon

corannulene

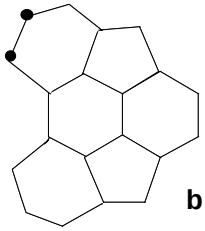


c

4 hexagons + 2 pentagons



a



b

stability order: a > b > c

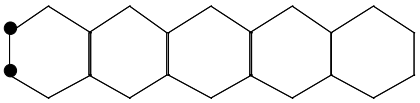
fig 1d

Clusters Si_2C_n in sp2 V

Si_2C_{20} - 26 bonds

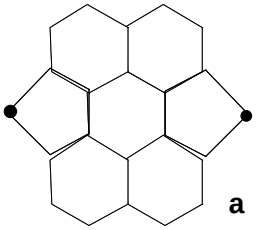
5 hexagons

pentacene

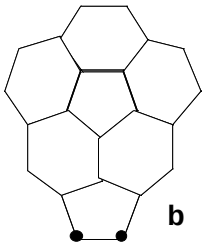


Si_2C_{20} - 28 bonds

5 hexagons + 2 pentagons



a



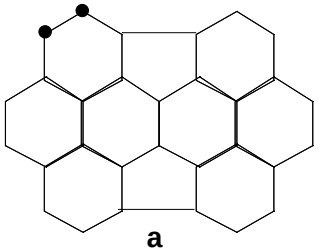
b

stability order: a > b

Si_2C_{28} - 39 bonds

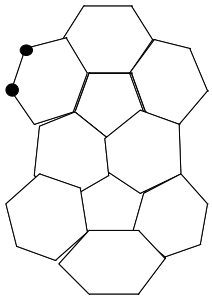
8 hexagons + 2 pentagons

Wakabayashi cluster #1



a

double corannulene
(half-fullerene)



b

stability order: a > b

fig1e

Fig. 1 : Clusters Si_2C_n in sp^2 hybridization. They are given the names of the corresponding hydrocarbons [10] ; let us recall that the clusters do not contain any hydrogen atom. The lacking H atoms are replaced here by "dangling bonds".

The number of bonds is indicated since only the electronic energies of the clusters can be taken into

account and compared for a given n and a given number of bonds (see text). The positions of the silicon atoms are shown by full circles.

Fig.1 a : Si_2C_n : n=3 to 10

Fig.1b : Si_2C_n : n=11 to 13

Fig.1c : Si_2C_{14}

Fig.1d : Si_2C_n : n=16, 18

Fig.1e : Si_2C_n : n=20, 28. For n=28 (a), Wakabahashi cluster is taken from ref [15]. 28 (b) has the structure of a half C_{60} fullerene.

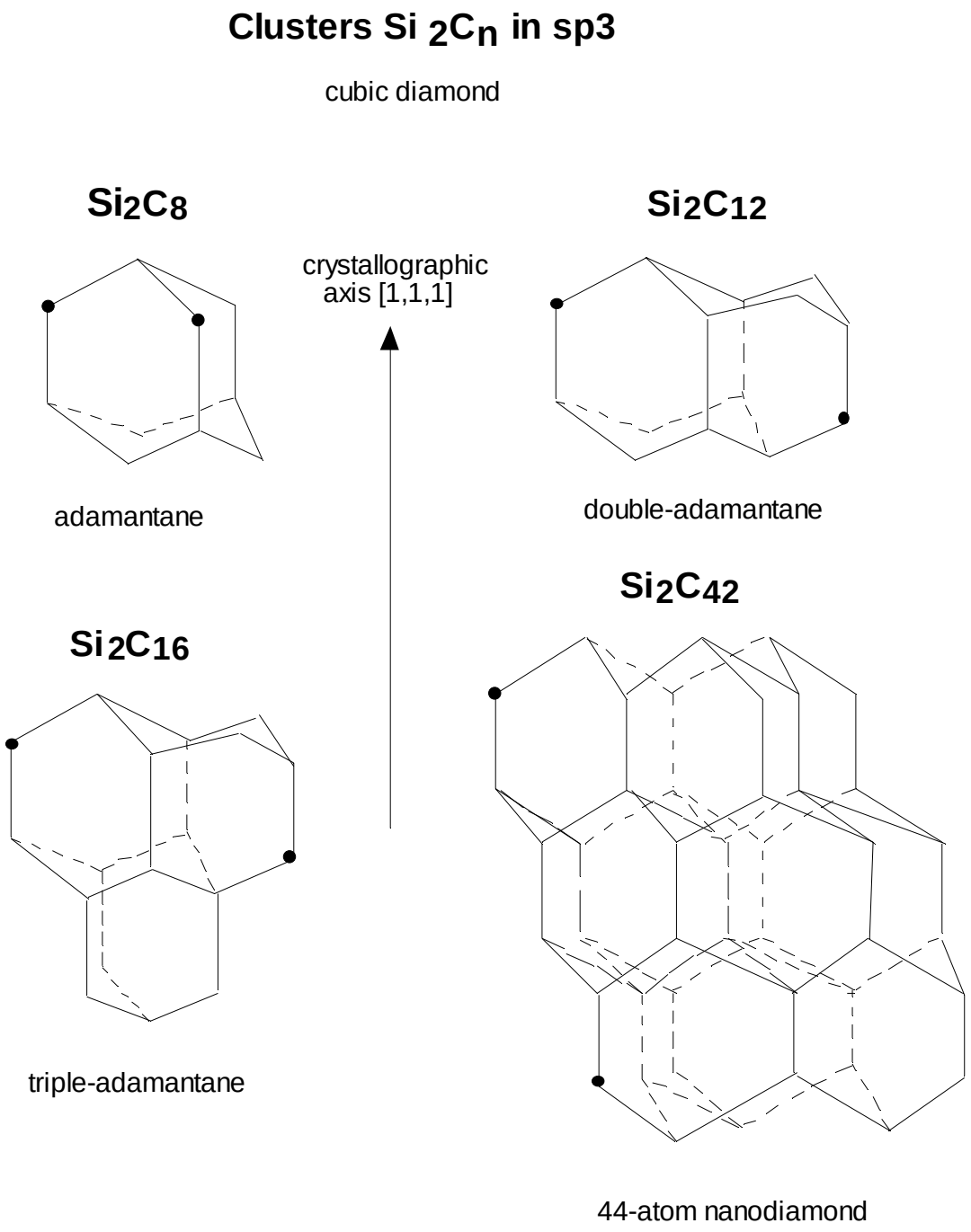
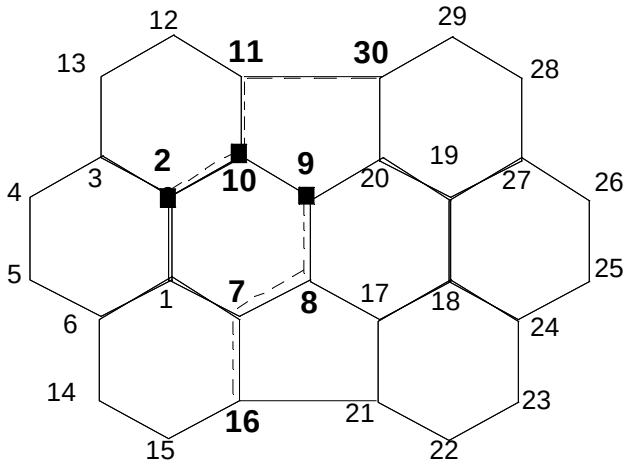


Fig. 2 : Clusters Si_2C_n in sp^3 hybridization (cubic lattice structure) : n=8 ("adamantane" without hydrogen atoms, taken from ref (Joyes [16]), n=12, 16, 42. The axis shows the direction [1,1,1] of the cubic lattice. Si atoms are shown by black circles.

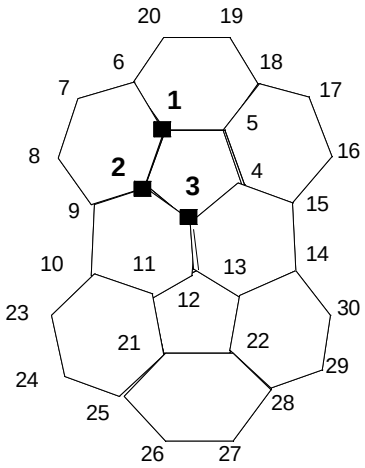
Simulation of very larger systems in sp2 hybridization

sp2

Si_2C_{28}

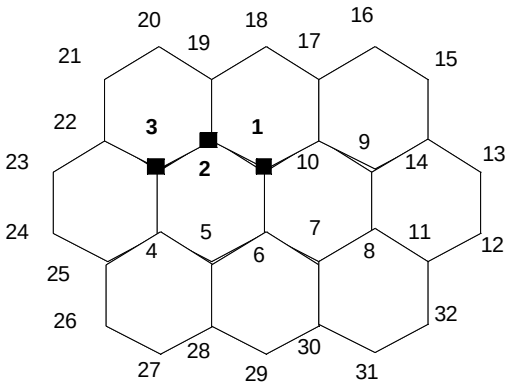


Wakabayashi cluster #1



double corannulene

(30-atom half-fuller**e**n)



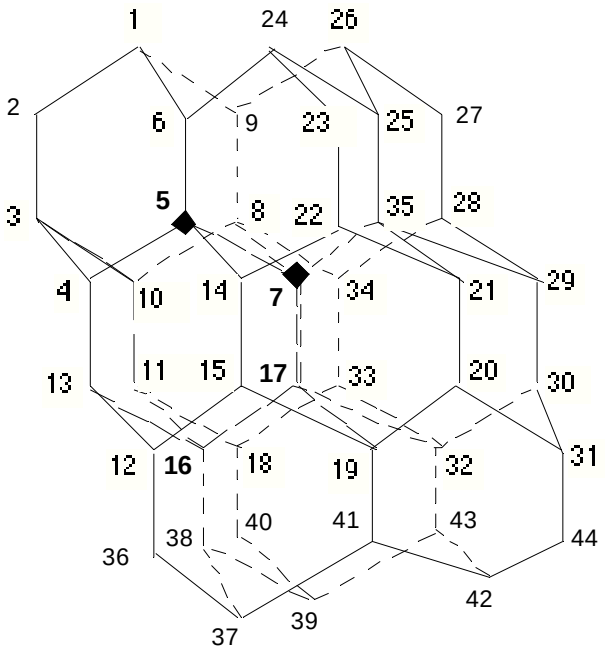
Si_2C_{30} ovalene

■ positions of Si atoms

Fig. 3 : Simulation of very larger systems in sp^2 hybridization in the cases of n=28 and n=30 "ovalene" which is a part of a plane of graphene. The full squares are the positions inside the clusters which are used as origins in the energy calculations of the 2 Si pairs. For instance, for n=28 (a), 9/8= 1st neighbours ; 9/7= 2nd neighbours along the path 9/8/7 ; 9/16= 3rd neighbours along the path 9/8/7/16 (in dashed lines).

Simulation of very larger systems in sp3 hybridization

sp3



44-atom nanodiamond

Fig. 4 : Simulation of very larger systems in sp^3 with the 44-atom nanodiamond. The cluster has only 2 inner atoms #7 and #17. The full rhombuses show the positions 7 or 5 (atoms "saturated" that is without dangling bonds) which play the rôle of origins in the energy calculations of the Si pairs.

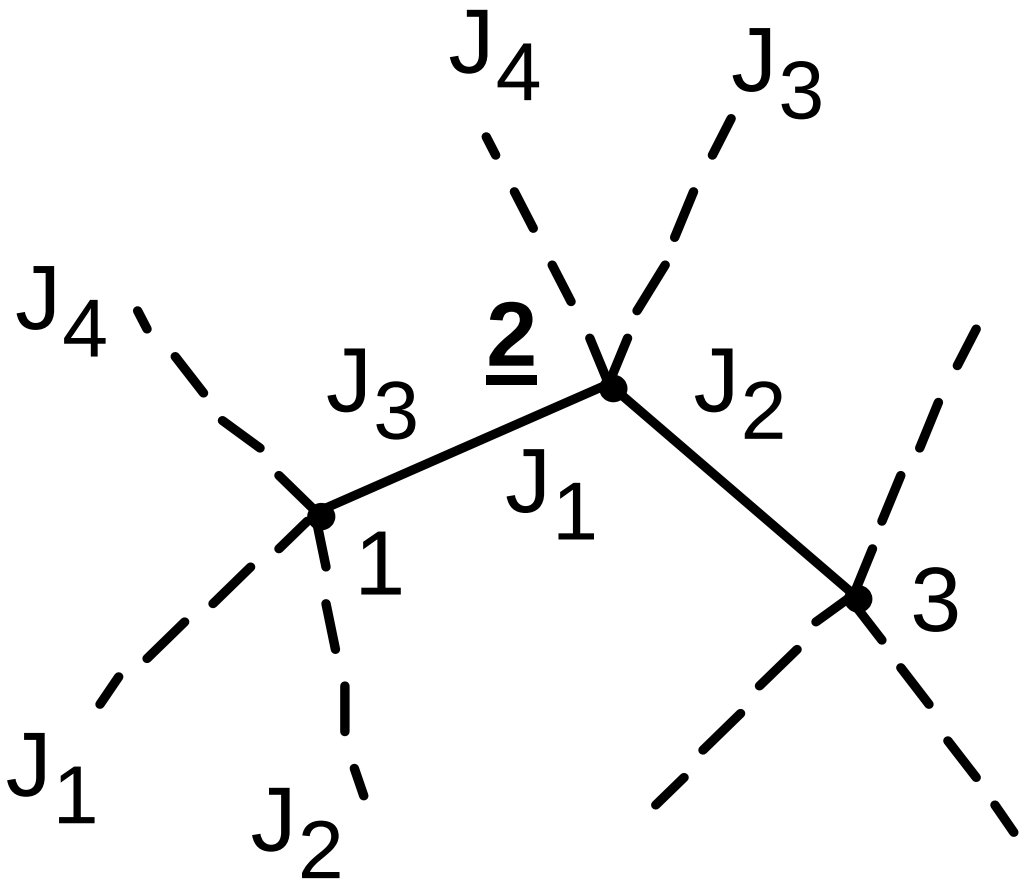


Fig. A1 : Hybrid orbitals | iJ> in sp^3 around sites #1, 2 or 3 (J= 1 to 4 on every site). Dangling bonds are in dotted lines.

J_1 = | 2 1> = hybrid orbital centered on site 2 along the 2-1 bond ; J_3= |1 3> = hybrid orbital centered on site 1 along the 1-2 bond.

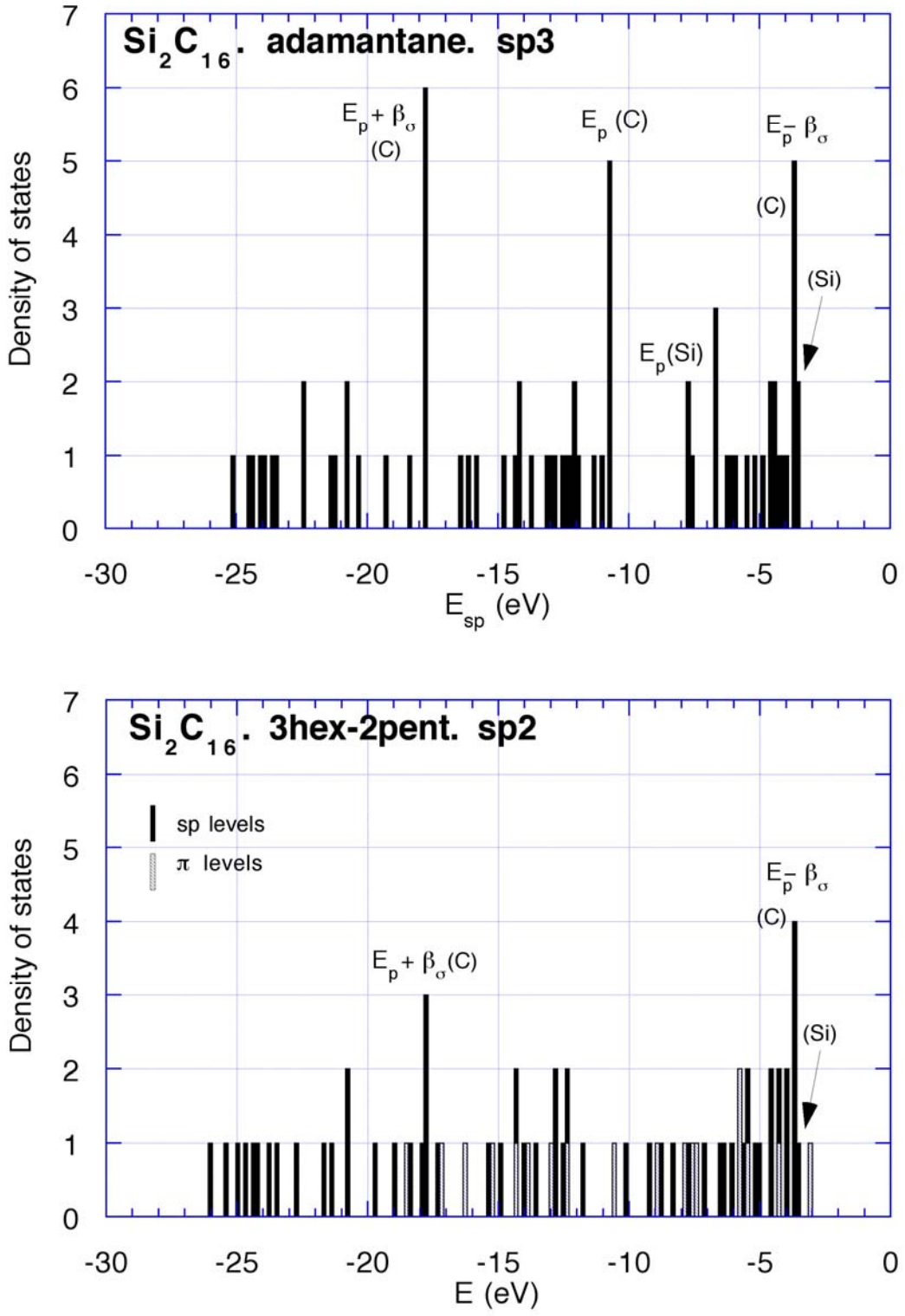


Fig. A2 : Density of states (DOS) for Si_2C_{16} in sp^3 (" triple adamantane") and sp^2 (shape (b) with 3 hexagons and 2 pentagons). In sp^3, there are only sp levels with a gap of forbidden energies between E_p(C) and E_p(Si) (see text). In sp^2, the solid lines show the sp levels and the hatched lines the π levels. In the energies $E_p \pm \beta_\sigma$, E_p and β_σ for C or Si are taken in absolute values.

Tables

Clusters as models of larger systems (sp2)

first neighbours		**second neighbours**			**third neighbours**			**Results**
pair	$\|E_1\|$ (eV)	pair	$\|E_2\|$ (eV)	ΔE_2 (eV)	pair	$\|E_3\|$ (eV)	ΔE_3 (eV)	
9/8	**2269.6613**	**9/7**	2268.87	**+ 0.790**	**9/1**	2268.81	**+ 0.852**	**$\Delta E_i > 0$**
					9/16	id		**more**
		9/17	id	**+0.790**	**9/18**	id	**+ 0.852**	**stable**
					9/21	2268.91	**+ 0.750**	**cluster**
								when
9/10	2269.195	**9/2**	2268.41	**+ 0.783**	**9/1**	2268.81	**+ 0.386**	**the 2**
					9/3	2268.03	**+ 1.159**	**Si atoms**
		9/11	2268.43	**+ 0.760**	**9/12**	- (2b. atom)	**-**	**are first**
					9/30	2268.435	**+ 0.760**	**neighbours**
2/1	2268.223	**2/6**	2267.41	**+ 0.809**	**2/5**	- (2b. atom)	-	**$\Delta E_2 > 0$**
					2/14	id	-	**Si 1st neigh.**
		2/7	2268.058	**+0.164**	**2/8**	2268.81	*- 0.586*	*$\Delta E_3 < 0$*
					2/16	2268.32	*- 0.099*	*more stable if the 2 Si are*
								3rd neighb.
2/3	2268.0122	**2/4**	-(2b. atom)	**-**				
		2/13	id	**-**				
2/10	2269.268	**2/9**	2268.412	**+ 0.856**	**2/8**	2268.81	**+ 0.459**	**$\Delta E_i > 0$**
					2/20	2268.56	**+ 0.706**	**Si2 1st**
		2/11	2268.22	**+ 1.043**	**2/12**	- (2b. atom)		**neighbours**
					2/30	2268.43	**+ 0.841**	

10/2	2269.268	**10/1**	2268.058	**+1.210**	**10/6**	2267.882	**+1.386**	**$\Delta E_i > 0$**
					10/7	2269.597	*- 0.329*	*$\Delta E_3 < 0$*
		10/3	2267.744	**+1.524**	**10/4**	- (2b atom)	-	
					10/13	id	-	
10/9	2269.195	**10/8**	2268.872	**+0.323**	**10/7**	2269.597	*-0.402*	
					10/17	2269.159	**+0.0360**	
		10/20	2268.235	**+0.960**	**10/19**	2268.562	**+0.6328**	
					10/30	2268.532	**+0.6626**	
10/11	2268.8984	**10/12**	-(2b. atom)	-				
		10/30	2268.532	**+0.366**	**10/20**	2^{nd} neigh.		
					10/29	-(2b. atom)	-	

Table 1 : 30-atom cluster of Wakabayashi [15] Si_2C_{28} in sp^2 hybridization. Table of the energies of Si pairs in first nearest neighbours, 2^{nd} nearest neighbours, and 3rd nearest neighbours

Clusters as models of larger systems (sp2)

first neighbours		**second neighbours**			**third neighbours**			**Results**
pair	$\|E_1\|$ (eV)	pair	$\|E_2\|$ (eV)	ΔE_2 (eV)	pair	$\|E_3\|$ (eV)	ΔE_3 (eV)	
3/2	2268.8320	**3/1**	2268.232	**+0.6000**	**3/5**	2nd neigh.		**$\Delta E_i > 0$ more stable cluster when the 2 Si atoms <u>are first neighbours</u>**
					3/6	2267.672	**+1.1599**	
		3/9	2268.026	**+0.8060**	**3/8**	- (2b. atom)	**-**	
					3/10	2267.817	**+1.0149**	
3/4	2268.8312	**3/5**	2268.231	**+0.6000**	**3/1**	2nd neigh.		
					3/18	2267.672	**+1.1592**	
		3/15	2268.026	**+0.8052**	**3/14**	2267.818	**+1.0132**	
					3/16	- (2b. atom)		
3/12	**<u>2269.2324</u>**	**3/11**	2268.596	**+0.6360**	**3/10**	2267.817	**+1.4153**	**$\Delta E_i > 0$ Si 1st neigh.**
					3/21	2268.890	**+0.3424**	
		3/13	2268.595	**+0.637**	**3/14**	2267.818	**+1.4144**	
					3/22	2268.890	**+0.3424**	
2/1	2268.9290	**2/5**	2267.896	**+1.0330**	**2/4**	2nd neigh.		
					2/18	2267.386	**+1.5426**	
		2/6	2267.430	**+1.4989**	**2/7** **2/20**	- (2b. atom)		
2/3	2268.8320	**2/4**	2268.573	**+0.8590**	**2/5**	2nd neigh.		**$\Delta E_i > 0$ <u>Si2 1st neighbours</u>**
					2/15	2268.191	**+0.6409**	
		2/12	2268.595	**+0.2370**	**2/11**	2268.790	**+0.0420**	
					2/13	2268.825	**+0.0069**	

2/9	2268.4190	**2/8**	- (2b. atom)					**$\Delta E_i > 0$**
		2/10	2267.983	**+0.4360**	**2/13**	- (2b. atom)		
					2/11	2268.7900	**-0.3710**	
1/2	2268.9290	**1/3**	2268.232	**+0.6970**	**1/4**	2nd neigh		**$\Delta E_i > 0$**
					1/12	2268.890	**+0.0390**	
		1/9	2267.936	**+0.9928**	**1/8**	- (2b. atom)		
					1/10	2267.949	**+0.9800**	
1/5	2268.5860	**1/4**	2267.896	**+0.6898**	**1/3**	2nd neigh		
					1/15	2268.091	**+0.4950**	**$\Delta E_i > 0$**
		1/18	2267.365	**+1.2206**	**1/17**	- (2b. atom)		
					1/19	id		
1/6	2267.8640	**1/7**	- (2b. atom)					
		1/20	id					

Table 2 : 30-atom half-fullerene Si2C28. Table of energies in the sp2 hybridization for Si pairs in first nearest neighbours, 2nd nearest neighbours, and 3rd nearest neighbours

Clusters as models of larger systems (sp2)

first neighbours		**second neighbours**			**third neighbours**			
pair	$\|E_1\|$ (eV)	pair	$\|E_2\|$ (eV)	ΔE_2 (eV)	pair	$\|E_3\|$ (eV)	ΔE_3 (eV)	**Results**
1/2	2416.7973	**1/3**	2416.0063	**+0.791**	**1/4**	2416.8320	*-0.0347*	**$\Delta E_i > 0$**
					1/22	2415.7010	**+1.0963**	**more**
		1/19	2415.6503	**+1.147**	**1/18**	-(2b. atom)		**stable**
					1/20	-(2b. atom)		**cluster**
								when
1/6	2417.0910	**1/5**	2416.2124	**+0.878**	**1/4**	2416.8320	**+0.259**	**the 2**
					1/28	2415.8770	**+1.214**	**Si atoms**
		1/7	2416.2130	**+0.878**	**1/8**	2416.8320	**+0.259**	**<u>are first</u>**
					1/30	2415.8762	**+1.2148**	**<u>neighbours</u>**
1/10	2416.7973	**1/9**	2416.0070	**+0.790**	**1/8**	2416.8320	*-0.0347*	**$\Delta E_i > 0$**
					1/14	2415.7020	**+1.0953**	**Si 1st neigh.**
		1/17	2415.6501	**+1.1472**	**1/16**	-(2b. atom)		
					1/18	-(2b. atom)		
2/1	2416.7973	**2/6**	2416.2130	**+0.584**	**2/5**	2417.2860	*-0.4887*	
					2/7	2416.9170	*-0.1197*	
		2/10	2416.1013	**+0.696**	**2/9**	2416.7832	**+0.0141**	
					2/17	2416.1420	**+0.655**	
2/3	**<u>2417.3250</u>**	**2/4**	2415.9910	**+1.334**	**2/5**	2417.2860	**+0.039**	**$\Delta E_i > 0$**
					2/25	2416.0710	**+1.254**	**<u>Si2 1st</u>**
		2/22	2415.0313	**+1.393**	**2/21**	-(2b. atom)		**<u>neighbours</u>**
					2/23	-(2b. atom)		
2/19	2416.2460	**2/18**	-(2b. atom)					
		2/20	-(2b. atom)					

3/2	**2417.3250**	**3/1**	2416.0063	**+1.3187**	**3/6**	2416.8320	**+0.493**	
					3/10	2416.7841	**+0.5409**	
		3/19	2415.7890	**+1.536**	**3/18**	-(2b. atom)		
					3/20	-(2b. atom)		
3/4	2416.6880	**3/5**	2415.9914	**+0.6966**	**3/6**	2416.8320	*-0.144*	
					3/28	2416.0160	**+0.672**	**$\Delta E_i > 0$**
		3/25	2415.7924	**+0.8956**	**3/24**	-(2b. atom)		
					3/26	-(2b. atom)		
3/22	2416.4960	**3/21**	-(2b. atom)					
		3/23	-(2b. atom)					

Table 3 : 32-atom ovalene in sp^2 hybridization : study of Si atom pairs built from atoms #1 or #2 or #3 (see fig.) (only 3-bond atoms, that is maximum connectivity according to the hybridization).

Clusters as models of larger systems (sp3)

first neighbours		**second neighbours**			**third neighbours**			**Results**
pair	$\|E_1\|$ (eV)	pair	$\|E_2\|$ (eV)	ΔE_2 (eV)	pair	$\|E_3\|$ (eV)	ΔE_3 (eV)	
7/5 **7/8** **7/35**	3328.695	**7/9** **7/10** **7/34**	(3b. atom)					
7/17	3328.7492	**7/16**	3329.147	- 0.3978	**7/11**	- (3b. atom)	-	$\Delta E_2 < 0$
					7/13		-	the 2
					7/38		-	**Si atoms**
		7/19	3329.147	- 0.3978	**7/15**	- (3b. atom)	-	are not
					7/20		-	first
					7/41		-	neighbours
		7/32	3329.145	- 0.3958	**7/30**	- (3b. atom)	-	
					7/33		-	
					7/43		-	
5/4 **5/6** **5/14**	- (3b. atom)							- - -
5/7	3328.695	**5/8**	3329.0151	- 0.3201	**5/9**	- (3b. atom)		$\Delta E_i < 0$
					5/10			the 2
					5/35			**Si atoms**
		5/35	id	- 0.3201	**5/21**	- (3b. atom)	-	are never
					5/25			first
					5/29			neighbours
		5/17	3329.1462	- 0.4512	**5/16**	3329.009	- 0.314	
					5/19	3329.010	- 0.315	

					5/32	3329.0583	- 0.3633	

Table 4 : 44-atom cluster nanodiamond: study of Si atom pairs built from atoms #7 or #5(only 4-bond atoms, that is atoms with maximum connectivity)

Appendix

A.1.Tight binding model with sp^ν hybridization

Let us remind that this is a one electron model, each electron moves in a mean potential V(r) which represents both the nuclei attraction and the repulsion of other electrons.σ and π electrons are separately treated :

1) Hamiltonian of σ bonds:

$| iJ >$: hybrid sp^ν orbital (ν=1,2,3) which points from site i along the bond J (Fig. A1).

If the molecular orbital σ is given by

$$|\psi> = \Sigma_{i,J}\, a_{iJ}\, | iJ > \qquad (1)$$

and the energy origin taken at the vacuum level, the Hamiltonian can be written as :

$$H_\sigma = E_m \Sigma_{i,J} \, | iJ >< iJ | \, + \, \Delta_\sigma \, \Sigma_{i,J,\, J'\neq J} \, | iJ >< iJ' | + \, \beta_\sigma \Sigma_{i,i'\neq i,J} \, | iJ >< i'J | \quad (2)$$

(i and i' are first neighbours) where E_m is the average energy: $E_m = (E_s - \nu E_p) / (\nu + 1)$,E_s and E_p are the atomic level energies,β_σ is the usual hopping or resonance integral in Hückel theory (interaction between nearest neighbour atoms along the bond),Δ_σ is a promotion integral (transfer between hybrid orbitals on the same site) : $\Delta_\sigma = (E_s - E_p) / (\nu + 1)$.

Remark: for an infinite crystal (bulk), the gap between valence and conduction band (forbidden

band) is $g = |-2\beta_\sigma + (\nu + 1)\Delta_\sigma|$ (for IVB elements) and β_σ can be derived from the values of g (5.33 eV for C, 1.14 for Si).

2) Hamiltonian of π bonds:

$$H_\pi = E_p \sum_i |i><i| + \beta_\pi \sum_{i,i'\neq i} |i><i'| \qquad (3)$$

with $|i>$: π orbital centered on atom i, β_π : hopping integral for π levels.

The β_π value for C was chosen in order to get the correct positions of C_2 energy levels in comparison to the results of the Verhaegen's ab initio calculation [18].

We need only 3 parameters: β_σ, β_π, and Δ_σ for the homonuclear model which represent in fact the average potential V(r) and which take into account the nuclear attraction and the dielectronic interactions[19]. But due to the fact that we only take into account on average the nuclear and dielectronic interactions, we can only compare clusters with the same number of atoms and the same number of bonds.

Tight binding parameters:

	C	**Si**
Es (eV)	- 19.45	- 14.96
Ep (eV)	- 10.74	- 7.75
βσ (eV)	- 7.03	- 4.17

$\beta\pi$ (eV)	- 3.07	- 0.8
Δ_σ (eV) sp2	- 2.90	-2.40
Δ_σ (eV) sp3	-2.18	-1.80

A.2.Density of states (DOS) : 2 examples of the density of energy levels are given in fig.A2 for the clusters Si_2C_{16}.

On top of figure A2, we show the triple adamantane in the sp^3 hybridization; therefore there are only sp or σ levels. We may see a flant band of p levels for the energy E_p(C) (here 5) and another one (with 2 levels) for the energy E_p(Si). Indeed, it is an heterocluster, which number of atoms is linked to the number of dangling bonds). We showed that for an homonuclear cluster, the number of p levels in the flat band E_p is N_c-n+s_a, where N_c (here 24) is the number of dangling bonds in the cluster with $N_c=(\nu-1)n+2(1-c)$ in hybridization sp^ν ,c is the number of independent cycles in the molecules (here 7) and s_a the number of saturated atoms that is with no dangling bond. Multiple levels also appear for the values $|Ep|+|\beta\sigma|$ (C) = 17.77 eV et $|Ep|-|\beta\sigma|$ (C) = 3.71 eV.

On the bottom of figure A2, we showed the case of Si_2C_{16} shape (b) in sp^2 hybridization . The sp levels are represented by the black lines and the π levels by dotted lines, on each side of the energy E_p. There is no more flat band of sp levels for the energy E_p because there are less cut bonds.